

## DISTRIBUTION OF ORGANIC CARBON IN BED SEDIMENTS OF MANOA STREAM, OAHU, HAWAII

DR. ROSS A. SUTHERLAND\*

*Geomorphology Laboratory, Department of Geography, University of Hawaii, 2424 Maile Way, Honolulu, HI 96822, USA*

*Received 19 January 1998; Revised 14 October 1998; Accepted 9 November 1998*

### ABSTRACT

Organic carbon (OC) associated with fluvial bed sediment plays an important role in biotic and abiotic processes operating within drainage basins. Increasingly, there is a need to characterize storage and spatial distributions of OC in aquatic sediments, particularly under-sampled areas like tropical streams. The objectives of this study were to examine in detail the variation of OC concentration with bed sediment grain size, to characterize the influence of grain size variation on relative OC mass storage, and to compare weighted OC values to those in other aquatic sediments worldwide.

The study area selected was a third-order dendritic drainage basin developed in a basaltic complex. Bed sediments along a 6 km section of Manoa Stream were systematically sampled every 50 m for a total of 113 sample site locations. Sediments were partitioned into six size fractions ( $< 2.0$  mm) and OC was determined by dry combustion. Data indicate that the OC concentration increases with decreasing grain size, with the greatest values in the  $< 0.063$  mm (silt + clay) fraction, approximately 4–6 times greater than the very coarse sand fraction (1.00–2.00 mm). Robust smoothing techniques illustrated a general decrease in OC concentration downstream for the size fractions  $< 0.25$  mm. Bed sediments were dominated by size fractions coarser than 0.5 mm (80 per cent of the total distribution) and only about 2 per cent in the fractions less than 0.13 mm. Combining information on OC concentration per size fraction and the mass contribution of each fraction to the whole sample, it was observed that fractions coarser than 0.5 mm had eight to 12 times the storage of OC per kilogram of bed sediments than the fractions finer than 0.13 mm. Weighted OC values for Manoa Stream were on average  $6.7 \text{ g-OC kg}^{-1}$ , and these were similar to those reported in the literature for a variety of sediments in aquatic environments, both freshwater and marine. These data provide important information on the relative mass storage of OC in bed sediments and their longitudinal patterns in a tropical fluvial environment. Copyright © 1999 John Wiley & Sons, Ltd.

KEY WORDS: fluvial bed sediments; organic carbon; grain-size partitioning; tropical stream; spatial patterns; Hawaii

### INTRODUCTION

The study of organic carbon (OC) in aquatic systems is an important area of investigation from the following perspectives: biogeochemical cycling, ecosystem energy, and storage and transport of pollutants. Transport of terrestrial carbon into streams, down rivers and eventually into the world's oceans is an important factor in balancing the global carbon budget (Hope *et al.*, 1994; Kao and Liu, 1996). At the scale of the drainage basin organic matter, and its primary constituent OC, plays an important role as an energy source in fluvial ecosystems (Boon, 1990; Bretschko, 1990), as an agent for storing and transporting trace elements and heavy metals (Horowitz, 1991), and sequestering or complexing hydrophobic toxic pollutants like polynuclear aromatic hydrocarbons (Evans *et al.*, 1990), DDD, DDE and dieldrin (Gilliom and Clifton, 1990). Additionally, Downing *et al.* (1993) note that carbon dynamics and storage in freshwater systems are sensitive to changes in land use, pollutant loads, climate, hydrologic conditions and atmospheric chemistry. Therefore these sediments constitute an important archive of environmental information.

---

\* Correspondence to: R. A. Sutherland, Geomorphology Laboratory, Department of Geography, University of Hawaii, 2424 Maile Way, Honolulu, HI 96822, USA. Email: sutherla@hawaii.edu  
Contract/grant sponsor: University of Hawaii at Manoa; contract/grant number: 3-89947

Despite the critical importance of OC in environmental process dynamics there have been only a limited number of detailed sedimentological or geomorphological studies of OC storage and its association with bed sediments in fluvial environments. Most data that are available on OC in aquatic bed sediments come from temperate systems. Mulholland and Elwood (1982) observed that the role of inland aquatic sediment as a carbon sink has largely been ignored. Though this statement is still true today, important advances, particularly in the biological and aquatic sciences, have been made, (e.g. Minshall *et al.*, 1983; Naiman *et al.*, 1987).

The importance of bed sediments has recently been stressed by Horowitz (1991), and he states that they should play an integral part of environmental studies examining geochemical cycles, reconnaissance surveys, spatial distributions, long-term temporal changes, and biological effects. Gagnier and Baily (1994) also note that sediment description is becoming an essential consideration in many types of lotic (flowing water environments) research. Relationships between aquatic sediments and OC have typically focused on the variation in concentration with particle size or on bulk samples without grain size partitioning. The results from aquatic grain size partitioning studies have been mixed, but many have found a typical increase in OC concentration with decreasing grain size (Choi and Chen, 1976; Horowitz, 1991), or increasing surface area (Mayer, 1994); but the relationship is commonly non-linear. On the other hand, some studies present a more complicated relationship of OC with particle size. Cammen (1982) found the OC concentration in one of four marine sediment samples to be greater in the  $> 67 \mu\text{m}$  fraction, while in the remaining samples the  $< 67 \mu\text{m}$  fraction dominated. Leichtfried (1985) found the highest OC concentration (0.58 per cent) in river bed sediments (0–20 cm depth) in the 0.5–1.0 mm fraction compared to 0.06 per cent in the 1.0–5.0 mm fraction, and 0.55 per cent in the fraction less than  $53 \mu\text{m}$ . Evans *et al.* (1990) found a bimodal distribution of organic matter (OM) concentration in river sediments with the highest values in the 1.0–2.0 mm fraction, followed by the  $< 0.13 \text{ mm}$  fraction, and the lowest values between 0.13 and 0.50 mm. Schorer (1997) also observed a bimodal distribution of OM concentration, with peaks in the fine silt fraction (2.0–6.3  $\mu\text{m}$ ) and in the very fine sand and fine sand fractions (63–200  $\mu\text{m}$ ). The reasons for the variations in OC concentration with grain size may be attributable to different types of OC, i.e. labile vs. refractory, and it may represent different ages and thus degree of humification and enzymatic processing. Regardless, this makes fluvial OC modelling based on grain size alone a very difficult proposition. Additionally, most aquatic sediment studies that have examined OC variation with grain size have only focused on concentration values, ignoring mass loading as a function of varying grain size proportions.

The objectives of this study are to examine, in detail, the partitioning of OC concentration with bed sediment grain size in a tropical perennial stream, to examine the influence of individual grain size fractions on the mass of OC stored over a 6 km channel length, and to explore the longitudinal distribution of bed sediment grain size and OC within Manoa Stream.

## STUDY DESIGN

The focus in this study on sampling and analysis of bed sediments is based on their ability to archive a variety of elements by adsorption (Mayer, 1994) and absorption (Horowitz, 1991). Additionally, bed sediments are closely linked to the quality of the overlying water column, both in terms of dissolved species and particulate matter.

### *Study site description*

The Manoa drainage basin, located in southeast Oahu (Figure 1), was used as the fundamental unit of investigation. Manoa Stream is one of 366 perennial streams on the five major Hawaiian islands (Stone, 1989). Manoa is a third-order perennial stream system that is typical of many urbanized basins in Hawaii, i.e. reasonably short distances from headwaters to outlet, dendritic in form, steep headwater sections and rather gentle lower reaches. The basin has a planimetric area of  $15.5 \text{ km}^2$ , and a total channel length of about 18.7 km, for a relatively low drainage density of  $1.2 \text{ km km}^{-2}$ . The bedrock is basalt and the basin is covered by six soil orders, in order of areal importance: Entisols  $>$  Inceptisol  $>$  Ultisols  $>$  Oxisols  $>$  Mollisols  $>$  Vertisols.

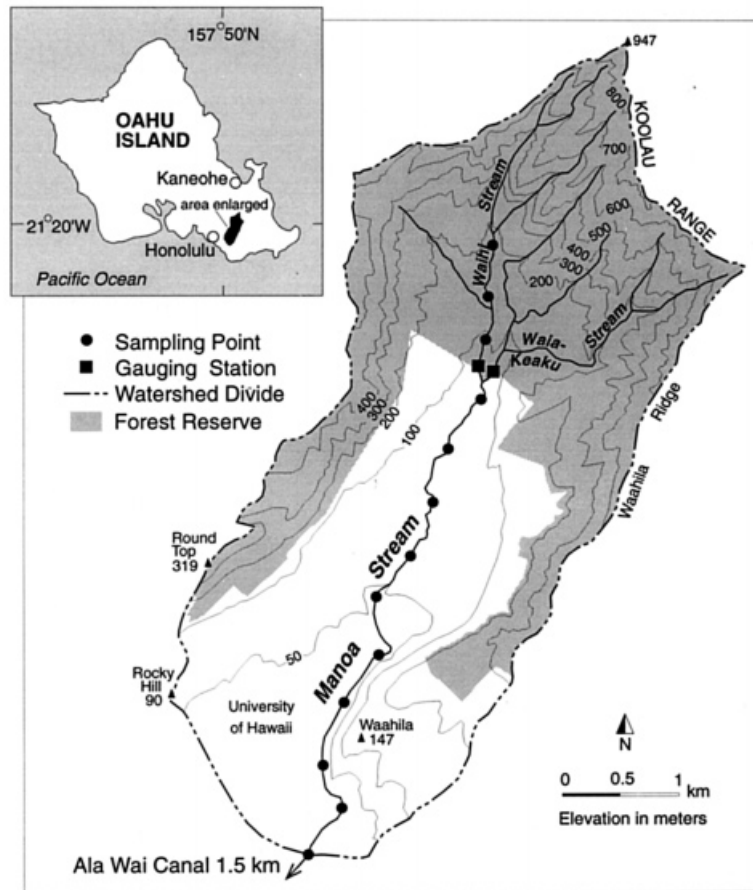


Figure 1. Study area location map, Manoa drainage basin, Oahu, Hawaii. Note that every tenth sample site is indicated by an large dot; this represents a distance of approximately 500 m

This urban basin is dominantly undisturbed above the two US Geological Survey (USGS) gauging stations (Figure 1) and is characterized by high annual rainfall values ( $> 1.5$  m) and dense tropical vegetation. Below the gauging stations there is a mix of residential, academic institutes, and commercial land uses. Typically Manoa is a confined channel, either naturally by steep valley side-walls or in some locations artificially by channelization, and thus has little associated floodplain. Manoa Stream is not unusual in that its channel morphology differs from its headwater sections to its outlet (cf. Simons and Simons, 1987). Above the gauging stations the channels have low sinuosity and are best described as having a cascade-type channel morphology (Montgomery and Buffington, 1997) composed typically of gravel and boulders. Within the cascade portion of the stream depositional locations of sands and gravels are associated with large obstacles, but their spatial extent is limited. Below the USGS stations the channel is more sinuous and is typically composed of a coarse sand and gravel mixture with large basalt boulders spalled from the surrounding valley walls. Depositional bars including point bars and obstacle-related mid-channel bars are frequent in the lower stream sections.

### *Sampling site distribution and collection strategy*

An equal-interval, systematic sampling design was used in this investigation. From the outlet of Manoa Stream samples were collected at 50 m intervals during baseflow conditions on three successive days. A total of 117 sites were included in the sampling array for a total distance approaching 6 km. Only samples from the main third-order channel and second-order segment of Waihi stream were collected. Samples for four locations could not be collected due to concrete (box-type) channelization at distances of 2.80–2.95 km from the outlet. The systematic sampling framework was used because it is easy to field operationalize after initially identifying a random starting point near the basin outlet. Additionally, Gilbert (1987) states that this sampling approach is usually the method of choice when estimating trends or patterns over space.

A clear 10 cm internal diameter Plexiglas tube sampler was used to collect three separate 5 cm cores at each sampling site. Cores were composited and double-bagged for transport to the laboratory. All samples were cold-stored at about 5°C prior to processing.

### *Sample processing*

Each composite sample was hand-sieved through a non-metallic 2 mm screen and only the fraction <2 mm was examined in this study. As noted by Napier (1993), it is likely that this size fraction contains most of the OC in the sediments. Additionally, this corresponds with the operational definition of soil scientists as stated by Nelson and Sommers (1982), that soil OM includes only those organic materials that accompany soil particles through a 2 mm sieve. Sediment was thoroughly mixed in a Teflon-covered pan and halved. Shells, shell fragments or other visible biotic fragments were removed prior to further processing. One half of each sample was archived in cold storage for future analyses, and the remainder was oven-dried at 105°C for 24 h. Representative samples were then sieved using a Ro-Tap sieve shaker to quantify the percentage contribution of each of the following six grain size fractions: 1.00–2.00 mm (0.00 to  $-1.00\phi$ , very coarse sand); 0.50–1.00 mm (1.00 to  $0.00\phi$ , coarse sand); 0.25–0.50 mm (2.00 to  $1.00\phi$ , medium sand); 0.13–0.25 mm (3.00 to  $2.00\phi$ , fine sand); 0.063–0.13 mm (4.00 to  $3.00\phi$ , very fine sand); and <0.063 mm ( $>4.00\phi$ , silt + clay). The  $>4.00\phi$  fraction was not further subdivided because it generally accounted for only a small percentage of the total sample mass, commonly <2 per cent.

### *Organic carbon determinations*

Following sieving, individual grain size fractions were ground to a fine powder in a Spectrex 8100 mixer mill using a tungsten carbide bowl and balls for 5 min (cf. Sutherland *et al.*, 1996). Each ground sample was split to form two subsamples of approximately 0.50 g. The methodology outlined by Hirota and Szyper (1975) and Krom and Berner (1983) was used to isolate the OC fraction of sediments. This involved analysing one untreated subsample by dry combustion using a Leco WR-112 induction furnace (Leco Corporation, 1985) plus accelerators to generate temperatures in excess of 1200°C, and analysis of liberated CO<sub>2</sub> by an infra-red detector. Standards of 0.88 per cent C were used to initially calibrate a day's batch of analyses, and every tenth sample was a standard. Additionally, 0.25 g samples of the National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 2704 (Buffalo River sediment) were periodically included throughout a batch (certified C content = 3.348 per cent). Leco measurements on SRM-2704 did not differ significantly from the certified value ( $p = 0.12$ ,  $n = 11$ ); however, minor drift was noted towards the end of a batch and this was corrected. Combustion of the untreated sample provides a measure of total carbon (TC), which includes organic and inorganic (carbonate) C. The remaining subsample was heated in a muffle furnace for 16 h at  $450 \pm 10^\circ\text{C}$  to remove OC. Following desiccation the treated sample was analysed using the Leco instrument to provide a measure of inorganic C. Organic carbon was estimated as a residual, that is TC minus inorganic C. Though a number of different chemical treatment methods exist to remove OC (e.g. Froelich, 1980; Nieuwenhuize *et al.*, 1994), the muffle furnace approach was adopted in this study. This method was adopted because of its relative ease, because it requires no dangerous or potentially corrosive chemicals, and based on the assumption that there would be negligible inorganic C in a tropical (non-agricultural) watershed. Additional support for this approach was gained from a simple experiment that indicated that carbon values for 10 randomly selected samples treated for 24 h using the concentrated HCl

vapour-phase method of Hedges and Stern (1984) and Mayer (1994) did not differ significantly from those treated in the muffle furnace ( $p = 0.075$ ). However, the muffle furnace method is not recommended for sediments with potentially high carbonate contents because OC is incompletely removed at temperatures typically used (cf. Gibbs, 1977).

#### *Analytical methods*

A total of 1356 carbon determinations were made to characterize OC concentration for 113 sample sites with six grain size fractions partitioned per site. One-way analysis of variance (ANOVA) was used to establish whether there were statistically significant differences between grain size fractions for OC concentration. Prior to ANOVA all OC data were  $\log_{10}$ -transformed to correct positive skewness and stabilize variance. If the F-ratio was statistically significant at an  $\alpha$ -level of 0.05 the Bonferroni/Dunn all means *post-hoc* multiple comparison test was implemented. Multiple comparison tests compare all possible pairs of treatment group medians or means, and are performed only after the null hypothesis of 'all medians or means are identical' has been rejected (Helsel and Hirsch, 1992). Since OC concentration per individual grain size fraction does not tell the whole story of OC accumulation in bed sediments, the OC mass associated with each fraction was determined from the following relationship:

$$OC_{\text{Mass}} = \frac{OC}{100} GS \quad (1)$$

where,  $OC_{\text{Mass}}$  represents the mass of organic carbon associated with a given bed sediment size fraction ( $\text{g-OC kg}^{-1}$ ),  $OC$  represents the organic carbon concentration of each individual grain size fraction (per cent), and  $GS$  represents the contribution of a given grain size fraction to all bed sediments  $<2$  mm in diameter ( $\text{g kg}^{-1}$ ). For a given sample site, summation of OC mass values for each of the six fractions will provide an estimate of the weighted OC mass associated with 1 kg of bed sediments. The weighted value can then be compared to other studies that have examined the OC of aquatic sediment samples only on a bulk sample basis.

Equation 1 was developed to overcome the typical problem encountered in some studies with the focus on chemical concentration data alone. For example, a given fraction of sediment may have an extremely high concentration of an element; however, the mass of the actual fraction examined may be extremely small. Therefore, its overall element mass contribution or flux may be minimal, and commonly dwarfed by error terms associated with other fractions. Values of OC mass were also  $\log_{10}$ -transformed and analysed using procedures outlined above.

To examine spatial trends in bed sediment grain size and in grain size-associated OC contents, the robust locally weighted regression smoother 'lowess' was used (locally weighted scatterplot smoother; Cleveland and Devlin, 1988). Lowess represents an exploratory data analysis tool, and is used to reduce noise in data and to examine the general underlying patterns in spatial or temporal data sets. Other advantages of the lowess technique include: clarity of presentation when several groups of information are plotted together on the same graphic; outliers have minimal impact on curve form; and this approach does not assume an *a priori* linear relationship between variables (cf. Helsel and Hirsch, 1992).

## RESULTS

#### *Grain size partitioning of carbon concentrations*

Analysis of variance indicated that there were no significant differences in inorganic C concentration with grain size fraction ( $p = 0.14$ , data not shown). Median concentrations were low, and ranged from 0.03 per cent for the coarse sand fraction to 0.09 per cent for the very fine fraction. Given their relative insignificance no other discussion is presented in this study.

Variations in OC concentration with grain size (Figure 2) indicate significantly higher values in the silt + clay fraction. Data also indicate a decrease in concentration with increasing grain size as commonly

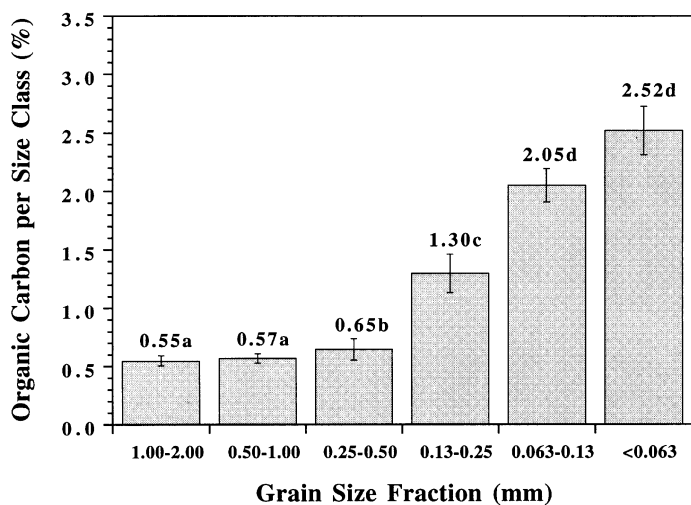


Figure 2. Partitioning of organic carbon concentration between six grain size fractions in bed sediments from Manoa Stream. Median values and 95 per cent confidence bands are plotted. Organic carbon values followed by the same letter are not significantly different at the  $\alpha$  0.05 level

suggested in the literature (e.g. Horowitz, 1991). No significant differences were observed between the very coarse and coarse sand bed sediment fractions. Since the  $<0.063$  mm fraction was not further subdivided, the peak in the fine silt fraction discussed by Schorer (1997) could not be corroborated for this tropical stream system. The higher concentrations of OC in the finest fractions can be attributed to a variety of processes including the increased potential for the formation of reasonably stable organo-mineral/colloidal complexes, increased production of biofilms, and increased abundance of condensed (aged) humic substances with decreasing grain size.

#### *Longitudinal variation in organic carbon concentration*

Results indicate some rather interesting spatial patterns of OC with distance from the basin outlet (Figure 3). For the three finest fractions (silt + clay, very fine and fine sand) there was a distinct decrease in concentration from the headwaters to the outlet, with the highest concentration in the forest reserve above the USGS gauging station. Medium sand showed a much more dampened pattern, but generally similar to the finer fractions. For the very coarse and coarse sand fractions there was no longitudinal pattern evident. The higher concentrations for grain size fractions  $<0.50$  mm in the headwaters reflect the direct contribution to the stream channel of OM from a closed riparian canopy. The primary contributor of OM to Manoa Stream is the riparian flora dominated by *Hibiscus tiliaceus*, *Macaranga tanarius*, *Schizostachyum glaucifolium* and *Musa* sp. (Shier, 1998). The contribution of OM from soil erosion along hiking trails in the headwaters may be a secondary source of OC in this area. Contributions of organisms to bed sediment OC could not be determined using the instrumentation described in this study. However, after flotation a macro-examination indicated mostly decayed, low density vegetative material.

#### *Grain size fractionation of bed sediments*

From Figure 4 it is evident that the  $<2$  mm bed sediment fraction was dominated by coarse and very coarse sands, accounting for about 83 per cent of the distribution. On average the very fine sand and silt + clay fractions account for only about 2 per cent of the distribution.

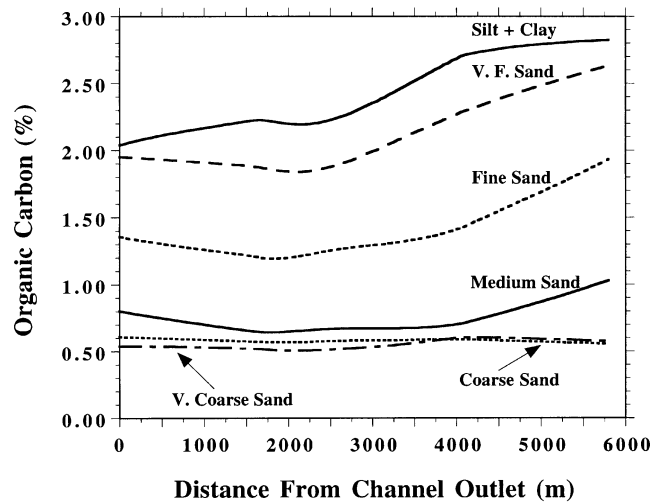


Figure 3. Longitudinal variation in organic carbon concentration for six grain size fractions for Manoa Stream bed sediments. A robust lowess smoother with a span of 25 per cent was used to fit the curves to the data so that the underlying spatial patterns could be captured

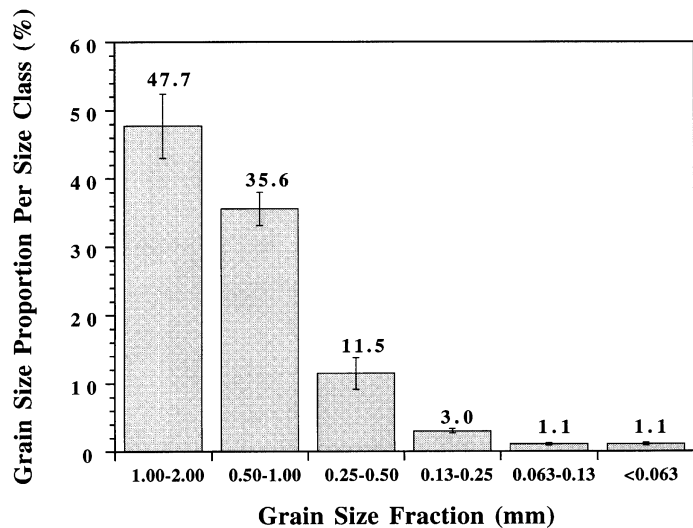


Figure 4. Distribution of six grain size fractions in Manoa bed sediments. Median values and 95 per cent confidence bands are plotted

For each sample location the geometric mean diameter was calculated for the bed sediments using the following equation:

$$GMD = \exp \left[ \frac{\sum_{i=1}^n w_i \log \bar{X}_i}{\sum_{i=1}^n w_i} \right] \quad (2)$$

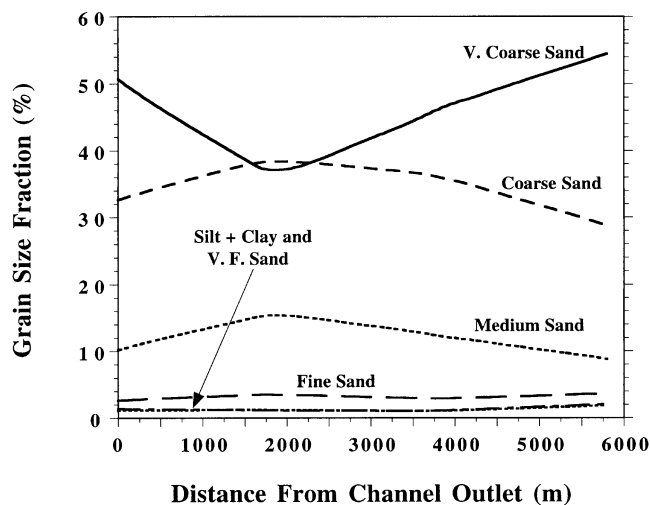


Figure 5. Longitudinal variation in six grain size fractions for Manoa bed sediments. A robust lowess smoother with a span of 25 per cent was used to fit the curves to the data so that the general spatial patterns could be discerned

where  $GMD$  is the geometric mean diameter (mm),  $w_i$  is the mass (g) of an individual size fraction,  $\bar{X}_i$  is the mean sieve size, and  $\sum_{i=1}^n w_i$  represents the total sample mass. The overall  $GMD$  for the 113 sites was  $0.92 \pm 0.09$  mm ( $\pm$  one standard deviation), and it exhibited reasonably low variation (coefficient of variation = 10 per cent, range 0.59 to 1.10 mm). Parametric regression was used to examine if there was any log-linear trend in  $GMD$  with distance from the basin outlet. Data indicated a non-significant increase from outlet to headwaters, with a positive correlation coefficient of 0.17 ( $p = 0.074$ ).

The longitudinal variation in individual grain size fractions from the outlet is shown in Figure 5. The three finest fractions show no significant longitudinal trends. Medium sand and coarse sand have similar patterns, with a gradual increase in percentage from the outlet to a distance of about 1800 m and a gradual decrease to the headwaters. The longitudinal pattern for very coarse sand showed a dramatic decrease from about 50 per cent in lower stream segments, near the outlet, to 35 per cent at 1800 m followed by an increase to values of 50–55 per cent in the upper sections sampled. A general decrease in the percentage of very coarse sand downstream was expected due to abrasion, fracturing and general comminution of bedload particles. However, the increase downstream of 1800 m was unexpected, but can be explained by residential construction and building of new facilities on the campus of the University of Hawaii. On several occasions the author observed illegal dumping of gravel and coarse sand within the channel from excavated material associated with construction activities. This material has been slowly reworked by the stream and has moved downstream as a series of bedform waves. Cobbles and boulders artificially added to the channel presently form small channel bank-welded bars in the lower reaches of the channel.

#### *Variation in organic carbon mass*

Equation 1 was used to compute the relative OC mass per grain size class (Figure 6). It is clear that the coarsest fractions contribute the greatest mass of OC to bed sediments  $<2.0$  mm. Statistical analyses indicate that OC mass contributions of coarse and very coarse sand are not significantly different, but are significantly greater than the finer fractions. The statistical ordering of OC storage is as follows: very coarse sand = coarse sand  $>$  medium sand  $>$  fine sand  $>$  silt + clay = very fine sand. It is also apparent from Figure 6 that soil or sediment investigations that simply focus on OC concentration data, ignoring grain size proportions, will provide a misleading picture of OC storage. The author is not aware of any other grain size partitioned OC mass data for aquatic sediments in the literature. Most data presented are based on bulk sample analyses (e.g.



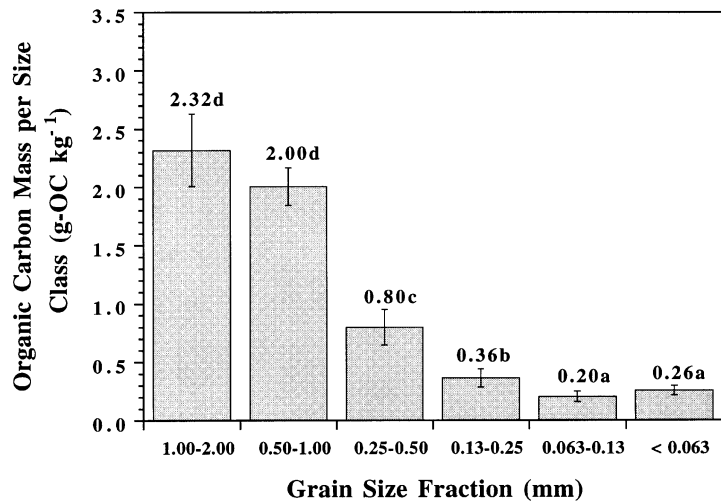


Figure 6. Variation in mass contributions of organic carbon to individual grain size fractions. Numeric values represent median values and error bars are 95 per cent confidence bands. Organic carbon values followed by the same letter are not significantly different at the  $\alpha$  0.05 level

Mayer, 1994) or concentrations for individual grain size fractions are given without corresponding grain size weighting (e.g. Leichtfried, 1985; Evans *et al.*, 1990; Schorer, 1997).

Organic carbon mass values for all grain size fractions were summed for a given sample site to calculate a weighted OC value. The histogram of weighted OC values (Figure 7) indicates a positively skewed (log-normal) distribution with a mean value of  $6.72 \pm 2.65$  g-OC kg<sup>-1</sup>, a median of 6.04 g-OC kg<sup>-1</sup>, and a range from 2.47 to 19.49 g-OC kg<sup>-1</sup>. Thus, on average a 1 kg bed sediment sample (< 2 mm) would contain a weighted average of 6.7 g of OC. These weighted OC values can be directly compared to literature values from aquatic sediment obtained from bulk sediment sampling. Though the study methods and environments vary appreciably it is clear from Table I that values from a small anthropogenically disturbed tropical stream are similar to those in a variety of other aquatic environments (freshwater and marine). In particular, the OC values from Manoa are most similar to those reported by Gilliom and Clifton (1990) for bed sediments of the San Joaquin River and its tributaries.

#### *Longitudinal pattern of weighted organic carbon*

The smoothed longitudinal distribution of weighted OC shows an interesting pattern, with a general decrease from headwater sections to the outlet of the drainage basin (Figure 8). Simpson *et al.* (1986) reported a reverse pattern, when they found that the OC of bulk samples along a 118 km section of the lower Hudson River progressively increased downstream. This was attributed to a decreased particle size of bed sediments with distance downstream, and presumably a greater potential for OC adsorption. Typical (smoothed) OC values indicate that 1 kg of bed sediments in headwater sections contain about 1.0–1.5 g-OC more than material near the basin outlet. This should not be interpreted as greater OC storage in the headwaters, and in fact the opposite would be the case in Manoa drainage basin. This paradox stems from discontinuous bed sediment accumulations in the headwaters, combined with a significantly smaller channel area and bankfull channel widths of <3 m. Downstream the bed sediment accumulations become more continuous, channel areas increase substantially with typical bankfull widths of 8 to 12 m. Additionally, a limited number of observations indicated that the bed sediment thickness was greater in the downstream reaches of Manoa Stream. Therefore, bed-associated total OC storage would decrease upstream because of significantly smaller volumetric accumulations of bed sediments. Decreased bed sediment accumulations with distance upstream have also been noted for another tropical (ephemeral) stream by Sutherland (1990) though no measurements of OC are available from this location.

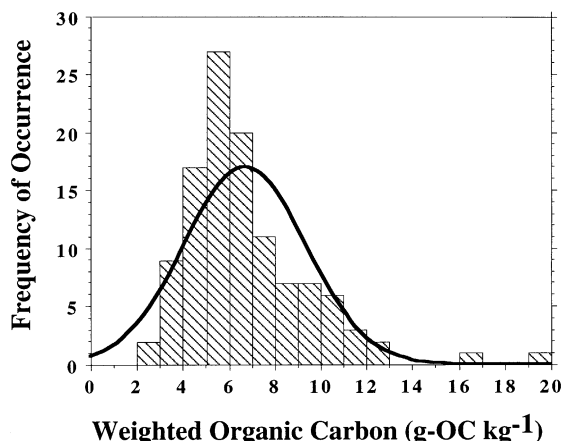


Figure 7. Frequency distribution of weighted organic carbon mass values for the 113 bed sediment sample sites in Manoa drainage basin. A normal curve is superimposed for comparative purposes

Table 1. Summary of organic carbon values for aquatic sediments

Reference	<i>n</i>	Mean (g-OC kg <sup>-1</sup> )	Median (g-OC kg <sup>-1</sup> )	Range (g-OC kg <sup>-1</sup> )	Bed sediment environment
de Haas & van Weering (1997)	8	-	-	3.5–17.1	Marine sediments, NE North Sea
Ergin <i>et al.</i> (1993)	166	-	-	3.7–21.6	Marine sediments, Sea of Marmara
Gilliom & Clifton (1990)	24	6.45 (4.87)*	5.55	0.5–17.0	San Joaquin River and tributaries
Karickhoff (1981)†	14	13.6	-	1.5–23.8	Freshwater sediments throughout the USA
Kelly & Hite (1981)†	258	46.0	-	3.0–142	63 lacustrine sediments from Illinois
Means <i>et al.</i> (1980)†	11	13.8	-	1.5–23.8	Freshwater fluvial sediments
Nieuwenhuize <i>et al.</i> (1994)	29	17.68 (14.95)	12.60	0.00–41.90	Marine sediments, various locations
Ritchie (1989)	58	19.0 (11.0)	-	3.0–56.0	Freshwater reservoir sediments, continental USA
Stein <i>et al.</i> (1994)	80	7.93 (4.28)	7.00	1.70–21.30	Marine sediments, Arctic Ocean
Suedel & Rodgers (1991)	102	13.6	5.7	0.3–118	Lake and reservoir sediments, continental USA
Suedel & Rodgers (1991)	76	11.4	2.4	0.2–63.5	Marine sediments, USA
This study	113	6.72 (2.65)	6.04	2.47–19.49	Freshwater sediments from Manoa Stream, Oahu, Hawaii

\* Values in parentheses represent  $\pm$  one standard deviation about the mean.

† Organic carbon values reported in these studies were tabulated in Suedel and Rodgers (1991).

## CONCLUSIONS

Speaker *et al.* (1984, p. 1840) state that: 'Rigorous, integrated investigations of relative patterns of transport, trapping and storage of both organic and inorganic matter are essential for the conceptual development of detrital dynamics in lotic ecosystems'. The present study is seen as compatible with the research directions identified by Speaker and colleagues. Bed sediments were the focus of this investigation as they are integral components of almost all alluvial stream channels and because they represent a sink and source of energy for aquatic organisms, nutrients and pollutants.

The bed sediments in Manoa Stream channel, a small, tropical perennial system, and their storage of OC were examined. All bed sediment samples were partitioned into six grain size fractions for 113 sites spaced at 50 m intervals. Organic carbon concentration for each of the grain size fractions was quantified by dry

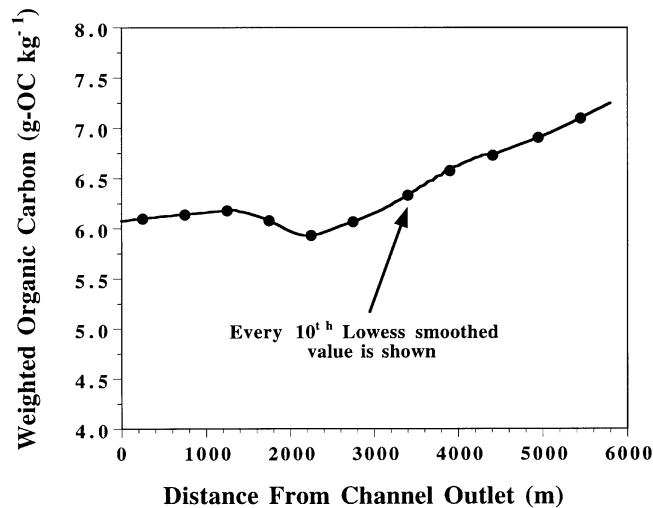


Figure 8. Longitudinal variation in weighted organic carbon mass in Manoa Stream bed sediments. A robust lowess smoother with a span of 25 per cent was used to fit a curve to the data, and every tenth data point is shown for clarity

combustion. Concentration data indicate a typical decrease in OC values with increasing grain size, with the highest values recorded in the silt + clay ( $<0.063$  mm) fraction (mean =  $2.5 \pm 0.6$  per cent, range = 1.3–4.1 per cent). These data can be compared to a mean of  $0.6 \pm 0.2$  per cent (range 0.3–2.0 per cent) for very coarse sand fraction (1.00–2.00 mm).

The longitudinal pattern of OC concentration data for grain size fractions finer than 0.50 mm indicated higher values in the headwater portions of Waihi Stream. No patterns were apparent for the OC associated with coarse and very coarse sand fractions. No other comparable data are available for Hawaii or other tropical systems. However, Manoa Stream is not a unique headwater system, with its major OC source being a closed riparian forest. This pattern is probably similar to most other headwater systems on the island of Oahu associated with the Koolau or Waianae mountain ranges. Biomass production is high in these areas due to annually warm temperatures and frequent rainfall from orographic lifting and cooling of the prevailing northeasterly trade winds.

Grain size analyses indicated that bed sediments were dominated by sediments between 0.5 and 2.0 mm. On average about 80 per cent of a given site was composed of coarse and very coarse sands. These data when combined with OC concentration data indicate that the coarsest fractions are the most important storage reservoirs for OC in the bed sediments of Manoa drainage basin. Typically the two coarsest fractions ( $>0.50$  mm) stored eight to 12 times more OC per kg than the two finest fractions ( $<0.13$  mm).

Average weighted OC values for Manoa bed sediments were  $6.7 \pm 2.6$  g-OC kg<sup>-1</sup> with a range from 2.5 to 19.5 g-OC kg<sup>-1</sup>. These values are some of the first detailed values reported for tropical drainage basins. Additionally, these weighted OC values are similar to those reported for a variety of fresh and marine aquatic sediments, particularly those for the San Joaquin River and its tributaries.

Spatial trend analysis indicated high OC values in the headwater sections of the watershed progressively decreasing towards the basin outlet. However, if a complete OC budget was to be computed for Manoa the increased volume of bed sediments downstream would overwhelm the mass stored in headwater channel segments.

#### ACKNOWLEDGEMENTS

This study was funded by a University of Hawaii at Manoa research grant no. 3-89947. Assistance with field sediment sampling by D. Ko and Dr Y. Wan is greatly appreciated. Professor Richard Green (University of

Hawaii, Department of Agronomy and Soil Science) kindly made his grinding equipment and LECO WR-112 analyser available for carbon determinations. The laboratory assistance of Dr C-T. Lee is much appreciated. Finally, the constructive comments of two anonymous reviewers were helpful in improving this manuscript.

## REFERENCES

- Boon, P. I. 1990. 'Organic matter degradation and nutrient regeneration in Australian freshwaters: II. Spatial and temporal variation, and relation with environmental conditions', *Arch. Hydrobiologia*, **117**(4), 405–436.
- Bretschko, G. 1990. 'The dynamic aspect of coarse particulate organic matter (CPOM) on the sediment surface of a second order stream free of debris dams (RITRODAT-LUNZ study area)', *Hydrobiologia*, **203**, 15–28.
- Cammen, L. M. 1982. 'Effect of particle size on organic content and microbial abundance within four marine sediments', *Marine Ecology-Progress Series*, **9**, 273–280.
- Choi, W.-W. and Chen, K. Y. 1976. 'Associations of hydrocarbons with fine particles and humic substances in nearshore surficial sediments', *Environmental Science and Technology*, **10**(8), 782–786.
- Cleveland, W. S. and Devlin, S. J. 1988. 'Locally weighted regression: An approach to regression analysis by local fitting', *Journal of the American Statistical Association*, **83**, 596–610.
- de Haas, J. and van Weering, T. C. E. 1997. 'Recent sediment accumulation, organic carbon burial and transport in the northeastern North Sea', *Marine Geology*, **136**, 173–187.
- Downing, J. P., Meybeck, M., Orr, J. C., Twilley, R. R. and Scharpenseel, H.-W. 1993. 'Land and water interface zones', *Water, Air, and Soil Pollution*, **70**, 123–137.
- Ergin, M., Bodur, M. N., Ediger, D., Ediber, V. and Yilmaz, A. 1993. 'Organic carbon distribution in the surface sediments of the Sea of Marmara and its control by the inflows from adjacent water masses', *Marine Chemistry*, **41**, 311–326.
- Evans, K. M., Gill, R. A. and Robotham, P. W. J. 1990. 'The PAH and organic content of sediment particle size fractions', *Water, Air, and Soil Pollution*, **51**, 13–31.
- Froelich, P. N. 1980. 'Analysis of organic carbon in marine sediments', *Limnology and Oceanography*, **25**(3), 564–572.
- Gagnier, D. L. and Bailey, R. C. 1994. 'Balancing loss of information and gains in efficiency in characterizing stream sediment samples', *Journal of the North American Benthological Society*, **13**(2), 170–180.
- Gibbs, R. J. 1977. 'Effect of combustion temperature and time, and of the oxidation agent used in organic carbon and nitrogen analyses of sediments and dissolved organic material', *Journal of Sedimentary Petrology*, **47**(2), 547–550.
- Gilbert, R. O. 1987. *Statistical Methods for Environmental Pollution Monitoring*, Van Nostrand Reinhold, New York.
- Gilliom, R. J. and Clifton, D. G. 1990. 'Organochlorine pesticide residues in bed sediments of the San Joaquin River, California', *Water Resources Bulletin*, **26**(1), 11–24.
- Hedges, J. I. and Stern, J. H. 1984. 'Carbon and nitrogen determinations of carbonate-containing solids', *Limnology and Oceanography*, **29**(3), 657–663.
- Helsel, D. R. and Hirsch, R. M. 1992. *Statistical Methods in Water Resources*, Elsevier Science, Amsterdam.
- Hirota, J. and Szyper, J. P. 1975. 'Separation of total particulate carbon into inorganic and organic components', *Limnology and Oceanography*, **20**(5), 896–900.
- Hope, D., Billett, M. F. and Cresser, M. S. 1994. 'A review of the export of carbon in river water: Fluxes and processes', *Environmental Pollution*, **84**, 301–324.
- Horowitz, A. J. 1991. *A Primer on Sediment-Trace Element Chemistry* 2nd edn, Lewis Publishers, Chelsea, MI.
- Kao, S.-J. and Liu, K.-K. 1996. 'Particulate organic carbon export from a subtropical mountainous river (Lanyang Hsi) in Taiwan', *Limnology and Oceanography*, **41**(8), 1749–1757.
- Krom, M. D. and Berner, R. A. 1983. 'A rapid method for the determination of organic and carbonate carbon in geological samples', *Journal of Sedimentary Petrology*, **53**(2), 660–663.
- Leco Corporation. 1985. WR-112 Wide Range Carbon Determinator, Model 788–600, Instruction Manual, Leco Corp., St Joseph, MI.
- Leichtfried, M. 1985. 'Organic matter in gravel streams (Project RITRODAT-LUNZ)', *Verhandlungen-Internationale Vereinigung fur Theoretische und Angewandte Limnologie (Proceedings-International Association of Theoretical and Applied Limnology)*, **22**, 2058–2062.
- Mayer, L. M. 1994. 'Surface area control of organic carbon accumulation in continental shelf sediments', *Geochimica et Cosmochimica Acta*, **58**(4), 1271–1284.
- Minshall, G. W., Petersen, R. C., Cummins, K. W., Bott, T. L., Sedell, J. R., Cushing, C. E. and Vannote, R. L. 1983. 'Interbiome comparison of stream ecosystem dynamics', *Ecological Monographs*, **53**, 1–25.
- Montgomery, D. R. and Buffington, J. M. 1997. 'Channel-reach morphology in mountain drainage basins', *Geological Society of America Bulletin*, **109**(5), 596–611.
- Mulholland, P. J. and Elwood, J. W. 1982. 'The role of lake and reservoir sediments as sinks in the perturbed global carbon cycle', *Tellus*, **34**, 490–499.
- Naiman, R. J., Melillo, J. M., Lock, M. A., Ford, T. E. and Reice, S. R. 1987. 'Longitudinal patterns of ecosystem processes and community structure in a Subarctic river continuum', *Ecology*, **68**(5), 1139–1156.
- Napier, I. R. 1993. 'The organic carbon content of gravel bed herring spawning grounds and the impact of herring spawn deposition', *Journal of the Marine Biological Association (United Kingdom)*, **73**(4), 863–870.
- Nelson, D. W. and Sommers, L. E. 1982. 'Total carbon, organic carbon, and organic matter', in Page, A. L. (Ed.), *Methods of Soil Analysis. Part 2: Chemical and Microbiological Properties*, 2nd edn, American Society of Agronomy and Soil Science Society of America, Madison, WI, 539–578.
- Nieuwenhuize, J., Maas, Y. E. M. and Middelburg, J. J. 1994. 'Rapid analysis of organic carbon and nitrogen in particulate materials', *Marine Chemistry*, **45**, 217–224.

- Ritchie, J. C. 1989. 'Carbon content of sediments of small reservoirs', *Water Resources Bulletin*, **25**(2), 301–308.
- Schorer, M. 1997. 'Pollutant and organic matter content in sediment particle size fractions', International Association of Hydrological Sciences, Publication No. **243**, 59–67.
- Shier, A. D. 1998. The Effect of Channelization and Clearing of Riparian Vegetation on Temperatures of Two Streams on the Island of Oahu, Unpublished Master of Arts Thesis, Department of Geography, University of Hawaii, Honolulu.
- Simons, D. B. and Simons, R. K. 1987. 'Differences between gravel- and sand-bed rivers', in Thorne, C. R., Bathurst, J. C., and Hey, R. D., (Eds), *Sediment Transport in Gravel-bed Rivers*, John Wiley and Sons, Chichester, 3–15.
- Simpson, K. W., Fagnani, J. P., Bode, R. W., DeNicola, D. M. and Abele, L. E. 1986. 'Surface area control of organic carbon accumulation in continental shelf sediments', *Journal of the North American Benthological Society*, **5**(1), 41–57.
- Speaker, R., Moore, K. and Gregory, S. 1984. 'Analysis of the process of retention of organic matter in stream ecosystems', *Verh. Internat. Verein. Limnol.*, **22**, 1835–1841.
- Stein, R., Grobe, H. and Wahsner, M. 1994. 'Organic carbon, carbonate, and clay mineral distributions in eastern central Arctic Ocean surface sediments', *Marine Geology*, **119**, 269–285.
- Stone, C. P. 1989. 'Hawaii's wetlands, streams, fishponds, and pools', in Stone, C. P. and Stone, D. B. (Eds), *Conservation Biology in Hawaii*, Cooperative National Park Resources Studies Unit University of Hawaii Press, Honolulu, 125–136.
- Suedel, B. C. and Rodgers, J. H. Jr. 1991. 'Variability of bottom sediment characteristics of the continental United States', *Water Resources Bulletin*, **27**(1), 101–109.
- Sutherland, R. A. 1990. 'Variability of in-channel sediment storage within a small semiarid (tropical) drainage basin', *Physical Geography*, **11**, 75–93.
- Sutherland, R. A., Watung, R. L. and El-waify, S. A. 1996. 'Splash transport of organic carbon and associated concentration and mass enrichment ratios for an Oxisol, Hawaii', *Earth Surface Processes and Landforms*, **21**, 1145–1162.